DRAWING AMENDMENT

Please replace the sole figure in this application with the amended drawing.

REMARKS

This amendment is submitted in an earnest effort to bring this case to issue without delay.

Applicants appreciate the Examiner's indication that claims 1 through 9 are allowable.

Applicants have canceled claim 10.

Applicants note that prosecution of this application on the merits is now closed and Applicants are submitting this amendment in order to make amendments to the specification and claim solely for the purpose of placing the application in better form to issue as a United States Patent. Applicants have not included any prohibited new matter in their amendments to the specification, claims and drawing.

Applicants have amended the specification to put in the proper headings employed in the preparation of a US Patent Application, to include a Brief Description of the sole figure in this application, and to amend Tables 1 through 5 to change the comma to periods for all of the values stated therein. The commas are used in European practice to indicate a decimal point, but of course in the United States a period is used. Applicants have also amended the tables to make sure that the headings at the top and the data appearing below are in proper alignment with one another.

Applicants have amended the drawing to indicate that the drawing is the sole Figure, rather than Figure 1, as required by US Patent Practice. In addition Applicants have amended the wording of Fraction S3, which results from the Transterification of Fraction M3 to obtain fatty acid methyl esters and other carboxylic acid methyl esters; see page 13, lines 3 through 9 of the specification for antecedent basis.

Applicants believe that the application, including all claims remaining therein, are in condition for allowance and a response to that effect is earnestly solicited.

Respectfully submitted,
K.F. Ross P.C.

By: Jonathan Myers, Re. 26,963
Attorney for Applicant

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5683 Riverdale Avenue Box 900
Bronx, NY 10471-0900
Cust. No.: 535
Tel: 718 884-6600
Fax: 718 601-1099
Email: *email@kfrpc.com*

Enclosure:
marked-up drawing in red
substitute drawing
marked up pages 1,5,8,16,18,
19,20, and 22 of spec in red

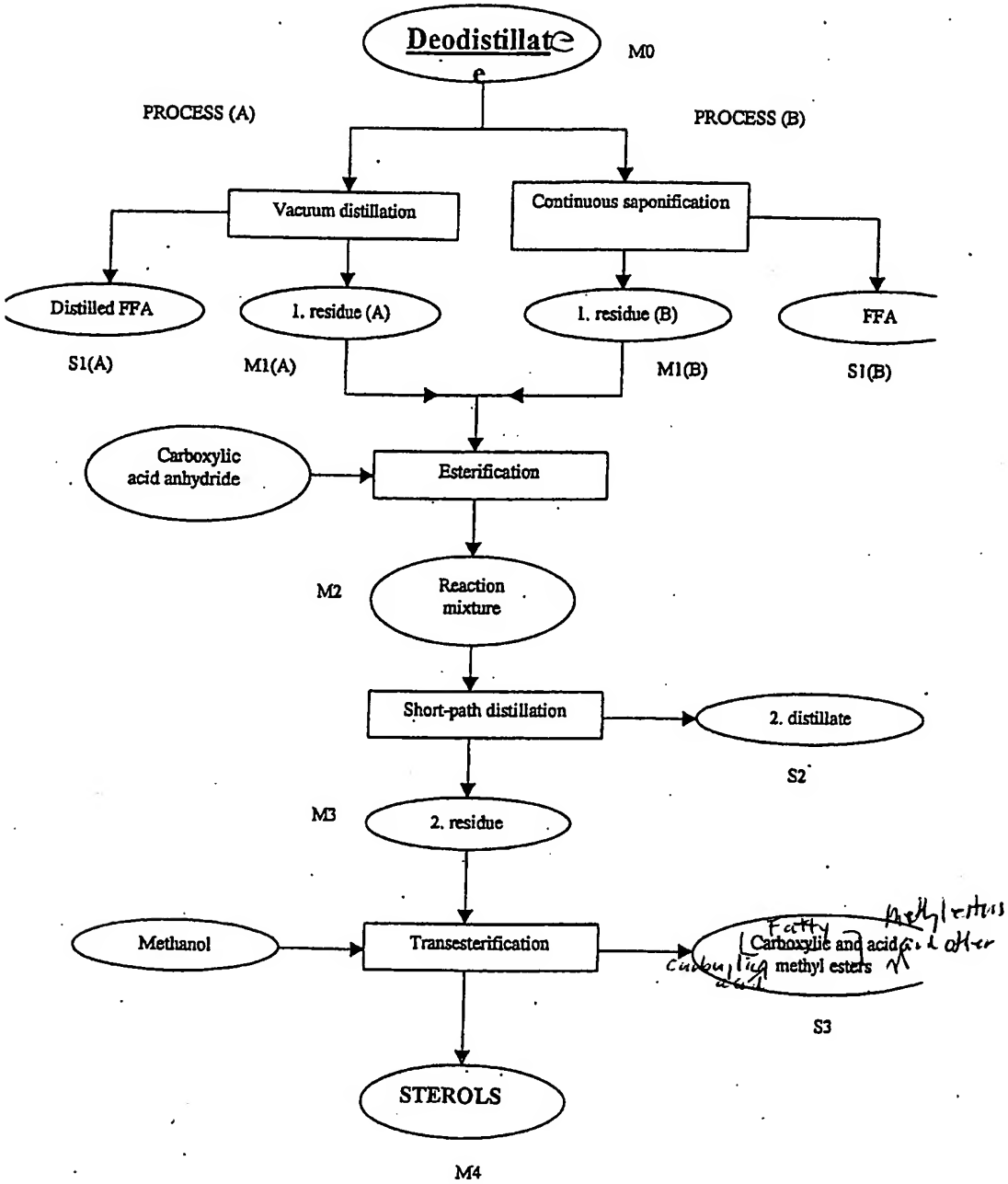

Figure 1

PROCESS FOR RECOVERY OF PLANT STEROLS FROM BY-PRODUCT OF VEGETABLE OIL REFINING

SPECIFICATION

Field of the Invention

The invention concerns the recovery of plant sterols and other valuable components such as tocopherols from a by-product of vegetable oil refining, deodorization distillate composed of sterols, sterol esters, tocopherols, fats or oils and their derivatives as well as fatty acids.

Background of the Invention

Occurring both in plants and animals, sterols are a group of natural compounds, the most important of which are summarised in the following table:

According to USP 5,512,691 prior to the fatty acid distillation, the free sterols are esterified with the fatty acids present in the deodorization distillate. The advantage of this step is that the boiling point range of the formed sterol esters is much higher than that of the unreacted tocopherols, which makes the separation of the two groups of compounds simple using short-path distillation.

According to USP 5,487,817 crystalline free sterols can be recovered from the sterol esters concentrated in the residue of the distillation.

Esterification of the free sterols with the free fatty acids present in the deodorization distillate requires relatively high temperature (150-250°C), long reaction time (1-12 hours) and reduced pressure (lower than 50 mbar), in some cases application of acidic type catalyst is necessary. As a consequence of the unfavourable conditions (high temperature, long reaction time), unwanted side-reactions take place, such as degradation of tocopherols, transformation of sterols into hydrocarbons by losing the functional -OH group and a H atom as water, and increased formation of tar.

Summary of the Invention

The process of the present invention for recovery of plant sterols and tocopherols from deodorization distillates formed during chemical or physical refining of vegetable oils, by distillation or saponification of the components present, can be characterised with the following steps:

In the process detailed in the invention, the raw material is a by-product of vegetable oil refining (deodorization) widely referred to as deodorization distillate, which can be originated from vacuum steam distillation of sunflower, rapeseed, soybean or corn oil. The deodorization distillate contains 2-15 weight% sterols and 30-85 weight% free fatty acids. When the deodorization distillate is a by-product of physical refining of vegetable oils, the free fatty acid content of the material is more than 50 weight% (typically 60-85 weight%). Removing firstly the free fatty acids from the deodorization distillate, we can decrease the quantity of the material at least by half. Consequently, we can decrease the size of the equipment necessary for the next reaction step.

The sterol fraction is predominantly composed of the following compounds: β-sitosterol, campesterol, stigmasterol, brassicasterol (only in case of rapeseed origin), and avenasterol. The free fatty acid fraction includes C14-C24 saturated and unsaturated fatty acids (among others myristic, palmitic, stearic, arachidic, behenic and lignoceric as saturated and myristoleic, palmitoleic, oleic, linoleic, linolenic, gadoleic and nervonic acid as unsaturated fatty acid). Besides the above components the deodorization distillates consist of mono-, di-, and triglycerides as well as tocopherols (1-8 weight%), tocotrienols, hydrocarbons, sterol esters and some other minor components.

Brief Description of the Drawing

The process according to the invention is demonstrated in the sole figure in the application which is a flow diagram of the steps of the process to recover plant sterols.

(Figure 1)

Table I.

Material code	M0		S1-A		M1-A	
Mass (gram)	1000		594,0		396,0	
Unit	%*	gram	%*	gram	%*	gram
Free fatty acid	62,34	623,40	92,25	547,97	18,76	74,29
Total tocopherol	2,07	20,65	0,51	3,04	4,41	17,46
Total sterol	3,29	32,86	0,51	3,05	7,42	29,37
Sterol esters	2,26	22,60	0,00	0,00	5,67	22,45
Glycerides	19,66	196,60	0,11	0,65	48,41	191,70

* the % values relate to weight%

Example 2

The same deodorization distillate (M0) as in Example 1 was used as starting material in the continuous solvent saponification reaction. The raw material (400 g) was dissolved in 2400 ml hexane. An alkali solution was made from 300 ml sodium hydroxide (concentration: 125 g/l), 400 ml water and 800 ml ethanol. This alkali solution was then added to the deodorization distillate - hexane solution and the mixture was intensively stirred for 5 min at room temperature. Afterwards the whole mixture was transferred into a

Material code	M0		S1-B		M1-B	
Mass (gram)	400		245,4		148,0	
Unit	%*	gram	%*	gram	%*	gram
Free fatty acid	62,34	249,36	98,74	242,31	0,49	0,73
Total tocopherol	2,07	8,26	0,00	0,00	5,08	7,52
Total sterol	3,29	13,14	0,41	1,01	7,63	11,29
Sterol esters	2,26	9,04	0,00	0,00	6,06	8,97
Glycerides	19,66	78,64	0,00	0,00	53,07	78,54

* the % values relate to weight%

Example 3

The residue of the first distillation of deodorization distillate (250 g M1-A) was treated with 11 g benzoic acid anhydride (90%, technical, Aldrich), we obtain free sterols from the sterol esters in this way.

Firstly the distillation residue was heated to 120°C and then, this temperature was maintained for 1 hour at 10 mbar residual pressure to remove the moisture traces. Afterwards the mixture was cooled to 80°C and the benzoic acid anhydride was added. The esterification reaction took place at a temperature of 150°C at 100 mbar residual pressure during 2 hours. The reaction was followed by

gas chromatographic (GC) analysis. In the end, we achieved 261 g reaction mixture (M2). The composition of the product is shown in Table III.

Table III.

Material code	M1-A		M2	
Mass (gram)	250,0		261,0	
Unit	%*	gram	%*	gram
Free fatty acid	18,76	46,90	15,83	41,32
Total tocopherol	4,41	11,02	4,10	10,69
Total sterol	7,42	18,54	0,00	0,00
Sterol esters	5,67	14,18	22,11	57,71
Glycerides	48,41	121,03	47,24	123,30

* the % values relate to weight%

Example 4

The esterified mixture (250 g M2) was treated in a short-path distiller (0.075 m^2) equipped with a heated jacketed dosing funnel and a control needle valve.

The operation resulted in a second distillate (44 g S2) and a second distillation residue (199 g M3). The distillate obtained in this step is the tocopherol concentrate. The composition of the distillation products is characterized in Table IV.

Table IV.

Material code	M2		S2		M3	
Mass (gram)	250,0		55,0		191,0	
Unit	%*	gram	%*	gram	%*	gram
Free fatty acid	15,83	39,58	66,47	36,56	1,14	2,18
Total tocopherol	4,10	10,25	18,56	10,21	0,00	0,00
Total sterol	0,00	0,00	0,00	0,00	0,00	0,00
Sterol esters	22,11	55,28	0,20	0,11	28,72	54,86
Glycerides	47,24	118,10	9,87	5,43	58,65	112,02

* the % values relate to weight%

Example 5.

In order to transesterify the sterol esters received in the short-path distillation step, firstly a solution composed of 100 ml methanol (water content: <0.02 weight%) and 10 ml sodium methylate (30% *w/w*) was made, then this solution was heated to its boiling point and

Table V.

Material code	S3		Material code	M4	
Mass (gram)	77,0		Mass (gram)	17,0	
Unit	%*	gram	Unit	%*	gram
Methyl esters**:	89,64	69,02	Brassicasterol	20,39	3,47
Free fatty acids	0,45	0,35	Campesterol	26,13	4,44
Total tocopherols	0,00	0,00	Stigmasterol	3,30	0,56
Total sterols	2,43	1,87	β-Sitosterol	42,92	7,30
Sterol esters	0,69	0,53	Other sterols	2,77	0,47
Glycerides	0,76	0,59	Total sterols	95,51	16,24

* the % values relate to weight%

** fatty acid- and other carboxylic acid methyl esters

For further purification of methyl-esters, first the traces of the catalyst and glycerol as well as other water-soluble components were removed by washing with water, then the washed material was dried and finally, pure methyl esters were obtained by vacuum distillation.